

■ ■ ■

**LA-UR--89-2486**

**DE89 015345**

A. '041. 12a 1.

J. W. SHAFER

1998, 1999, 2000, 2001, 2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009, 2010, 2011, 2012, 2013, 2014, 2015, 2016, 2017, 2018, 2019, 2020, 2021, 2022, 2023, 2024, 2025, 2026, 2027, 2028, 2029, 2030, 2031, 2032, 2033, 2034, 2035, 2036, 2037, 2038, 2039, 2040, 2041, 2042, 2043, 2044, 2045, 2046, 2047, 2048, 2049, 2050, 2051, 2052, 2053, 2054, 2055, 2056, 2057, 2058, 2059, 2060, 2061, 2062, 2063, 2064, 2065, 2066, 2067, 2068, 2069, 2070, 2071, 2072, 2073, 2074, 2075, 2076, 2077, 2078, 2079, 2080, 2081, 2082, 2083, 2084, 2085, 2086, 2087, 2088, 2089, 2090, 2091, 2092, 2093, 2094, 2095, 2096, 2097, 2098, 2099, 2100, 2101, 2102, 2103, 2104, 2105, 2106, 2107, 2108, 2109, 2110, 2111, 2112, 2113, 2114, 2115, 2116, 2117, 2118, 2119, 2120, 2121, 2122, 2123, 2124, 2125, 2126, 2127, 2128, 2129, 2130, 2131, 2132, 2133, 2134, 2135, 2136, 2137, 2138, 2139, 2140, 2141, 2142, 2143, 2144, 2145, 2146, 2147, 2148, 2149, 2150, 2151, 2152, 2153, 2154, 2155, 2156, 2157, 2158, 2159, 2160, 2161, 2162, 2163, 2164, 2165, 2166, 2167, 2168, 2169, 2170, 2171, 2172, 2173, 2174, 2175, 2176, 2177, 2178, 2179, 2180, 2181, 2182, 2183, 2184, 2185, 2186, 2187, 2188, 2189, 2190, 2191, 2192, 2193, 2194, 2195, 2196, 2197, 2198, 2199, 2200, 2201, 2202, 2203, 2204, 2205, 2206, 2207, 2208, 2209, 2210, 2211, 2212, 2213, 2214, 2215, 2216, 2217, 2218, 2219, 2220, 2221, 2222, 2223, 2224, 2225, 2226, 2227, 2228, 2229, 2230, 2231, 2232, 2233, 2234, 2235, 2236, 2237, 2238, 2239, 2240, 2241, 2242, 2243, 2244, 2245, 2246, 2247, 2248, 2249, 2250, 2251, 2252, 2253, 2254, 2255, 2256, 2257, 2258, 2259, 2260, 2261, 2262, 2263, 2264, 2265, 2266, 2267, 2268, 2269, 2270, 2271, 2272, 2273, 2274, 2275, 2276, 2277, 2278, 2279, 2280, 2281, 2282, 2283, 2284, 2285, 2286, 2287, 2288, 2289, 2290, 2291, 2292, 2293, 2294, 2295, 2296, 2297, 2298, 2299, 2300, 2301, 2302, 2303, 2304, 2305, 2306, 2307, 2308, 2309, 2310, 2311, 2312, 2313, 2314, 2315, 2316, 2317, 2318, 2319, 2320, 2321, 2322, 2323, 2324, 2325, 2326, 2327, 2328, 2329, 2330, 2331, 2332, 2333, 2334, 2335, 2336, 2337, 2338, 2339, 2340, 2341, 2342, 2343, 2344, 2345, 2346, 2347, 2348, 2349, 2350, 2351, 2352, 2353, 2354, 2355, 2356, 2357, 2358, 2359, 2360, 2361, 2362, 2363, 2364, 2365, 2366, 2367, 2368, 2369, 2370, 2371, 2372, 2373, 2374, 2375, 2376, 2377, 2378, 2379, 2380, 2381, 2382, 2383, 2384, 2385, 2386, 2387, 2388, 2389, 2390, 2391, 2392, 2393, 2394, 2395, 2396, 2397, 2398, 2399, 2400, 2401, 2402, 2403, 2404, 2405, 2406, 2407, 2408, 2409, 2410, 2411, 2412, 2413, 2414, 2415, 2416, 2417, 2418, 2419, 2420, 2421, 2422, 2423, 2424, 2425, 2426, 2427, 2428, 2429, 2430, 2431, 2432, 2433, 2434, 2435, 2436, 2437, 2438, 2439, 2440, 2441, 2442, 2443, 2444, 2445, 2446, 2447, 2448, 2449, 2450, 2451, 2452, 2453, 2454, 2455, 2456, 2457, 2458, 2459, 2460, 2461, 2462, 2463, 2464, 2465, 2466, 2467, 2468, 2469, 2470, 2471, 2472, 2473, 2474, 2475, 2476, 2477, 2478, 2479, 2480, 2481, 2482, 2483, 2484, 2485, 2486, 2487, 2488, 2489, 2490, 2491, 2492, 2493, 2494, 2495, 2496, 2497, 2498, 2499, 2500, 2501, 2502, 2503, 2504, 2505, 2506, 2507, 2508, 2509, 2510, 2511, 2512, 2513, 2514, 2515, 2516, 2517, 2518, 2519, 2520, 2521, 2522, 2523, 2524, 2525, 2526, 2527, 2528, 2529, 2530, 2531, 2532, 2533, 2534, 2535, 2536, 2537, 2538, 2539, 2540, 2541, 2542, 2543, 2544, 2545, 2546, 2547, 2548, 2549, 2550, 2551, 2552, 2553, 2554, 2555, 2556, 2557, 2558, 2559, 2560, 2561, 2562, 2563, 2564, 2565, 2566, 2567, 2568, 2569, 2570, 2571, 2572, 2573, 2574, 2575, 2576, 2577, 2578, 2579, 2580, 2581, 2582, 2583, 2584, 2585, 2586, 2587, 2588, 2589, 2590, 2591, 2592, 2593, 2594, 2595, 2596, 2597, 2598, 2599, 2600, 2601, 2602, 2603, 2604, 2605, 2606, 2607, 2608, 2609, 2610, 2611, 2612, 2613, 2614, 2615, 2616, 2617, 2618, 2619, 2620, 2621, 2622, 2623, 2624, 2625, 2626, 2627, 2628, 2629, 2630, 2631, 2632, 2633, 2634, 2635, 2636, 2637, 2638, 2639, 2640, 2641, 2642, 2643, 2644, 2645, 2646, 2647, 2648, 2649, 2650, 2651, 2652, 2653, 2654, 2655, 2656, 2657, 2658, 2659, 2660, 2661, 2662, 2663, 2664, 2665, 2666, 2667, 2668, 2669, 2670, 2671, 2672, 2673, 2674, 2675, 2676, 2677, 2678, 2679, 26

ATRAPT AND DIPRO INTERNATIONAL CONFERENCE ON HIGH PRESSURE SCIENCE AND TECHNOLOGY

1994

HIGH PRESSURE LABORATORY

WILLIAM PAPERBOOK.

REMARK 4.2. By the same argument, we can show that the following conditions are equivalent:

## DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees makes any warranty expressed or implied or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

[illegible]

1. The first group of variables is the set of variables that are used to define the population. These variables are: age, sex, race, and education. These variables are used to define the population because they are the most common variables used to define a population. These variables are also used to define the population because they are the most common variables used to define a population.

Los Alamos National Laboratory  
Los Alamos, New Mexico 87545

15182

**J. W. Shaner**  
**Los Alamos National Laboratory**  
**Los Alamos, New Mexico 87545 USA**

The recent discovery of a solid-solid phase change in shock-compressed Mo and the theoretical interpretation suggest valence d-electron density as a major influence on structural stability. The relationship of this experimental result to the transition metal structures and alloy phase diagrams will be discussed. Specific predictions will be presented for the locations and slopes of transition metal and transition metal alloy phase boundaries.

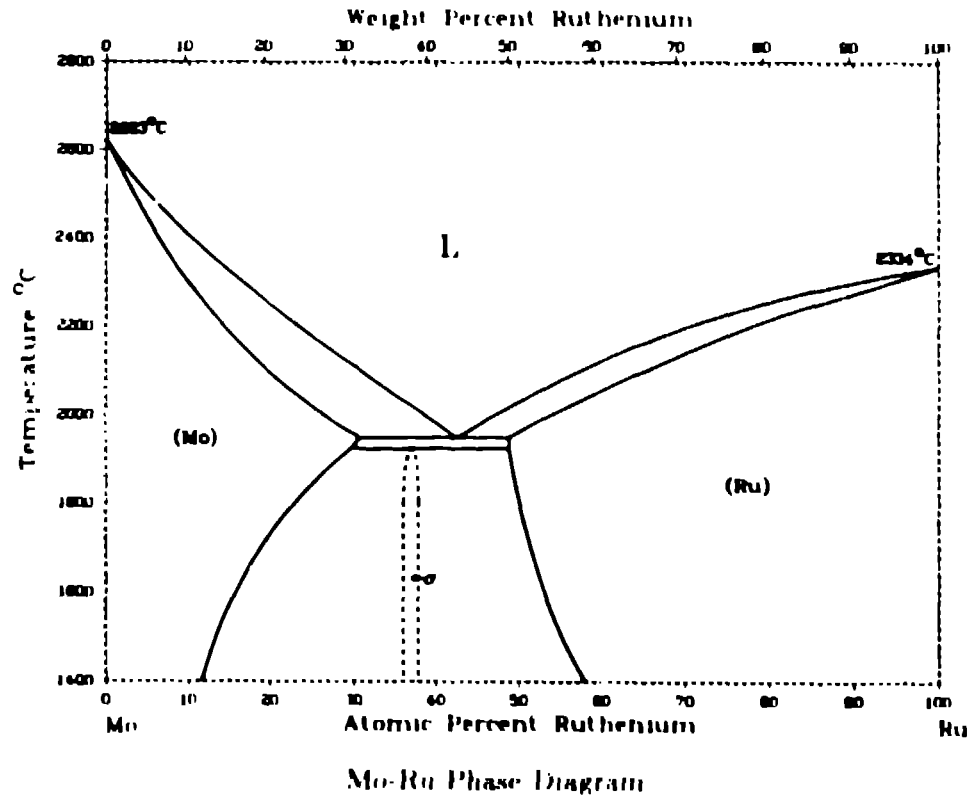
## Transition metals, phase transition

Skriver has shown through detailed LMTO calculations that the phase stability of the transition metals is dependent on the conduction d-electron density (Skriver, 1985). He shows that the stability of the bcc phase for group-V and VI transition metals at low temperature and pressure is dependent on having between 2.5 and 5 d-like electrons per ion. The group-VI metals Cr, Mo, and W need roughly 0.5 more d-electron per ion to cause stabilization of a close-packed phase, while the group-IV metals need only a small increase in d-electron occupancy to cause stabilization of the bcc phase.

Another recent calculation confirming the d-electron occupation dependence of phase stability has been presented for Re (Watson et al., 1998). APW calculations show that as pressure is increased on Re, causing the shift from s-like to d-like conduction electrons, the  $\beta$ -phase remains stable, in contrast to the suggestion that

This work was supported by the U.S. Department of Energy.

there may be a high-pressure bcc phase. On the basis of the unhybridized band calculations one expects pressure to drive Re away from the region of stability for bcc.



At the high temperatures and pressures in a strong shock, phase stability calculations must include all the terms in the Gibbs free energy. In particular the phonon entropy term which stabilizes the bcc structure at high temperature is important (Annamali, 1967). The electron entropy term will be generally smaller so long as  $T < 0.1 T_F$ , the Fermi temperature. Using a rigid band model, this term which is proportional to the density of states at the Fermi surface favors the bcc structure except for systems with six valence electrons per atom (Moruzzi, 1978). The other term in the free energy differences,  $P\Delta V$ , will also become important at sufficiently high pressures. Another complication in the very high pressure phase diagram is the hybridization of the s and d bands at pressures high enough that all valence electrons behave s-like. We expect again to stabilize the bcc lattice (Hoover et al., 1972).

Table I

Alloy	Atomic % Solute	Conduction Electrons Per Ion
Mo-Ti	50	6.5
Mo-Ru	30	6.6
Mo-Rb	20	6.6
Mo-Pd	7	6.3
W-Re	37	6.4
W-Os	19	6.4
W-Ir	10	6.3
W-Pt	5	6.2

We have shown that experiment and theory consistently suggest that d-electron occupation plays a dominant role in crystal structure stability and thermodynamics of transition metals. These observations suggest several more theoretical and experimental tests of the underlying physics. We know, for example that the hcp-bcc boundary for the group-IV elements, Ti, Zr, and Hf has a negative  $dP/dT$ . This suggests that pressure stabilizes the bcc phase along an isotherm, consistent with the increase in d-band occupancy. However, the other terms in the Gibbs free energy should be evaluated to show whether this phenomenon is really d-electron determined. Also, since alloying and pressure appear to have the same effect on structural stability by alloying Mo with Ru or W with Re, for example, one should force the bcc-hcp phase boundary to lower pressures, where it may be accessible to techniques other than strong shock loading.

## REFERENCES

- Annabali, A. E. F., Phys. Rev. 161, 445 (1967)
- Brown, J. M., J. W. Shaner, and C. A. Swenson, Phys. Rev. B32, 4507 (1985)
- Hixson, R. S., D. A. Boness, J. W. Shaner, and J. A. Moriarty, Phys. Rev. Lett. 62, 637 (1989)
- Hoover, W. G., D. A. Young, and R. Grover, J. Chem. Phys. 56, 2207 (1972)
- McMahan, A. K., Physica 139 & 140B, 31 (1986)
- McMahan, A. K., H. I. Skriver, and B. Johansson, Phys. Rev. B23, 5016 (1981)
- T. B. Massalski, Ed., Binary Alloy Phase Diagrams, American Society of Metals (1986)
- Moruzzi, V. L., J. E. Janak, and A. R. Williams, Calculated Electronic Properties of Metals, Pergamon Press, NY (1978)
- Watson, R. E., J. W. Davenport, M. Weinert, and G. Fernando, Phys. Rev. B38, 7817 (1988)